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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PS 3238 for a patent by THE UNIVERSITY OF NEWCASTLE RESEARCH ASSOCIATES LIMITED as filed on 27 June 2002.

WITNESS my hand this
Eighth day of July 2003

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AUSTRALIA

PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:-

"TOUGHENING OF THERMOSETS"

The invention is described in the following statement:-

This invention relates to the toughening of thermosets and has been devised particularly though not solely for application to epoxy resins.

Thermosets, such as epoxy resins, are brittle compared to thermoplastics because of their cross-linked molecular structures. Attempts have been made in the past to increase the toughness of thermosets, particularly epoxies, using the addition of liquid rubber or hard particles.

Liquid rubber has been successfully used as a toughening agent to increase the specific fracture energy. Its toughening mechanisms include bridging, cavitation, crack pinning, crack blunting etc. In addition to liquid rubber, other toughening agents such as hard particles, hard hollow microspheres and coreshell rubber have also been used.

Another development in this area is an attempt to toughen thermoplastics using a similar method to the one used for ceramics in which toughness increase was achieved by a volume dilatation in the vicinity of crack tip resulted from tetragonal to monoclinic phase transformation.

The present invention results from the realisation that the pre-stressing of the epoxy matrix, and the creation of residual compressive stress may be performed using expandable hollow microspheres and heat treatment to achieve a similar effect to that of the phase transformation of ceramics.

Accordingly, the present invention provides a method of manufacturing thermosets including the steps of adding expandable hollow microspheres to the base thermoset components in the liquid phase, and applying heat treatment to the mixture so formed, causing the microspheres to expand during, or after, curing of the thermoset.

Notwithstanding any other forms that may fall within its scope, one preferred form of the invention will now be described by way of example only, with reference to the

accompanying drawing which is a graph of the volume incremental expansion of microspheres due to heating.

In the preferred form of the invention, a thermoset in the form of an epoxy resin is toughened by the addition of expandable hollow microspheres, but it will be appreciated that this method can be applied to any other form of thermoset material.

A conventional resin system such as the resin system consisted of West System Epoxy 105 (a blend of Bisphenol A and Bisphenol F) and West System Slow Hardener 206 (a blend of aliphatic amines and aliphatic amine adducts based on diethylene triamine and triethylenetetramine) as curing agent, has a typical density of 1.1 for the resin system.

The system can be modified by the addition of expandable hollow microspheres as demonstrated in the following example.

Modifier used was hollow micro-spheres (EXPANCEL, 551 DU40, Akzo Nobel) which consist of co-polymer shell and gas. The chemical structure of the microspheres was found to be $(C_5H_8O_2\text{-}C_3H_3N\text{-}C_2H_2Cl_2)_x$ using a Perkin Elmer Fourier Transform Infra Red Spectrometer, Paragon 1000. The microspheres expand when heated. By way of example, microspheres were put in a 100 ml measuring cylinder and tapped for 5 minutes and then placed in an oven pre-heated to 70°C. Further heating of the oven followed every 5 to 6 minutes for an increment of 10°C until it reached 200°C. Resulting volume expansion of the microspheres measured as a function of temperature is shown in the accompanying diagram.

In a typical method of manufacture, a quantity of microspheres are added to the epoxy component and stirred for approximately ten minutes. The mixture is then heated to approximately 85°C for thirty minutes to reduce the viscosity for easy stirring before being allowed to cool gradually e.g. in a water bath for about half an hour. The curing agent is then added and stirred for five minutes.

The mixture can then be poured into a casting mould and left to cure at room temperature.

It has been found that epoxy resins toughened in this manner by the addition of expandable hollow microspheres and subsequently heated exhibit increased fracture toughness compared with simple epoxy resins of similar construction. It has been found that the heat treatment improves interfacial bonding between microspheres and the matrix. Compressive residual stress around microspheres, which may be responsible for the major toughening mechanism, is successfully created by hollow microspheres with the heat treatment. It has been found that specific fracture energy of epoxy can be increased about 13 times by this method.

DATED This 27th Day of June, 2002
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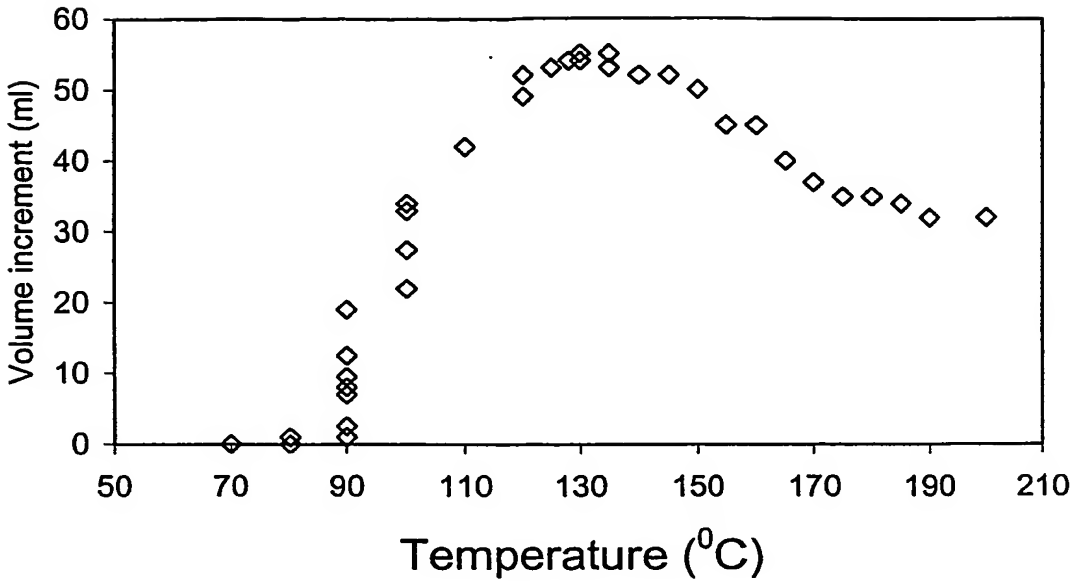
Volume increment (ml)
60
50
40
30
20
10
0
50
70
90
110
130
150
170
190
210
Temperature (^{0}C)